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*solutions that transform*

# FLUIDIZED BED GASIFICATION FOR CONVERSION OF BIOMASS AND WASTE MATERIALS TO RENEWABLE HYDROGEN

*Project DE-FE0032176*

John Marion, Sr. Director Carbon Management & Conversion- *GTI Energy*

$H_2$ Annual Merit Review Meeting May 6-9, 2024 – Crystal City, VA

# GTI Energy Overview

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*We occupy a unique space between **tradition** and **innovation***

- Moving energy systems solutions from **concept to market**
- Where partners go to **de-risk experimentation**
- Expertise in integrated systems and **low-carbon gases, liquids, infrastructure and efficiency**

**Valued Partners**

**175+**

80+ years of experience and leadership in energy production, storage, delivery and use

**Research & Development**

**$1B+**

In the past decade

Leading and convening collaborative R&D

**Innovation & Commercialization**

**1,300+**

Patents

**500**
Products

**750+**
Licensing Agreements

**10+** Industry Collaboratives

OTD
UTD
ETP Emerging Technology Program
LCRI LOW-CARBON RESOURCES INITIATIVE
PROJECT ASTRA
HYDROGEN TECHNOLOGY CENTER
$CH_4$ COLLABORATORY
H2@Scale
HyPER
VERITAS
OPEN HYDROGEN INITIATIVE

# We develop, scale and deploy solutions in the transition to low-carbon, low-cost energy systems

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## GTI Energy is a leading energy research and training organization

SOURCE · MAKE · MOVE · STORE · USE


**500+** Enterprise Employees

TOP WORK PLACES 2019 · 2020 · 2021 · 2022 · 2023 – Chicago Tribune

We work collaboratively to address critical energy challenges impacting gases, liquids, efficiency and infrastructure

OTD – Operations Technology Development

UTD – Utilization Technology Development

ETP – Emerging Technology Program

LCRI – LOW-CARBON RESOURCES INITIATIVE

# GTI Energy Gasification Heritage

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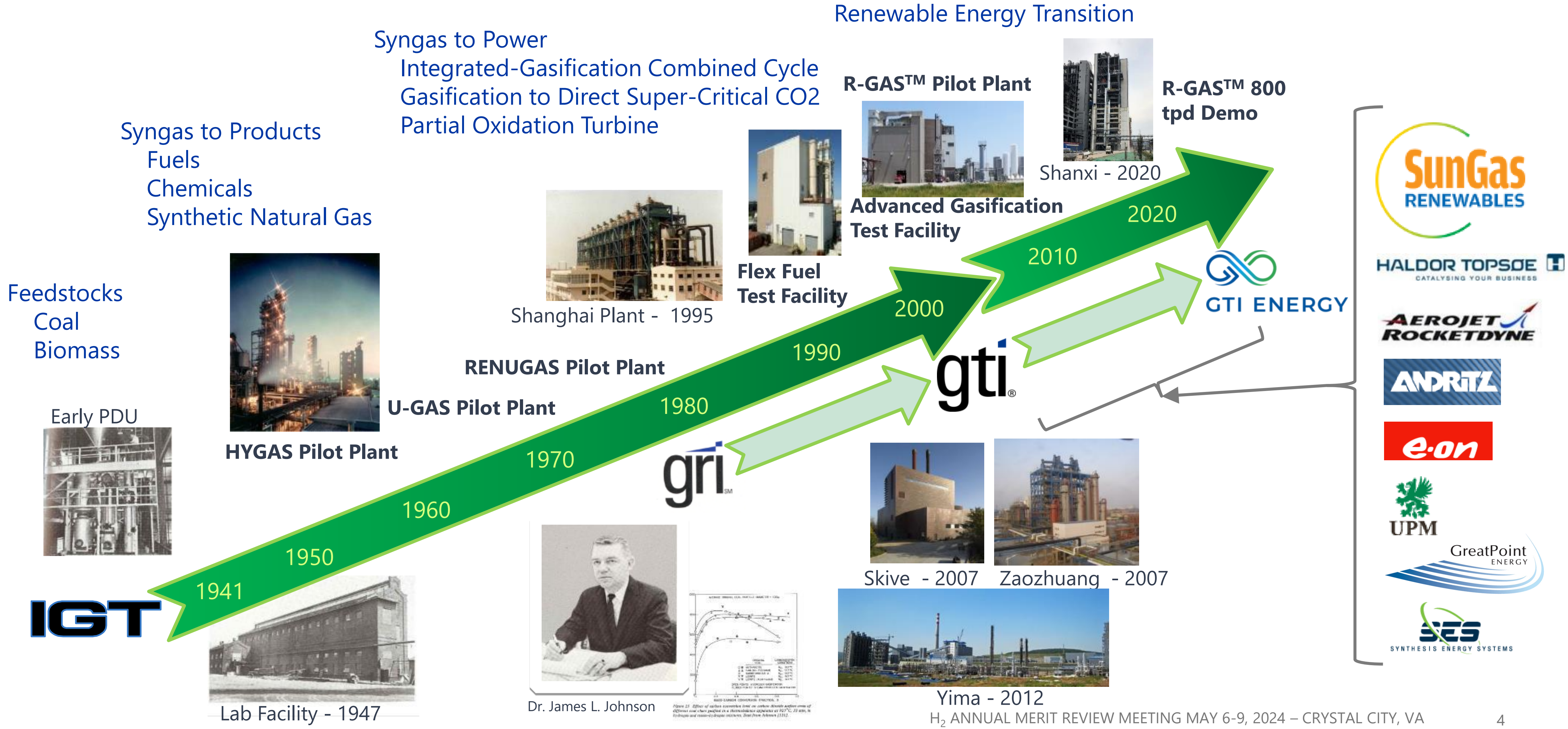

# Process Concept - Biomass and Waste Materials to Renewable Hydrogen

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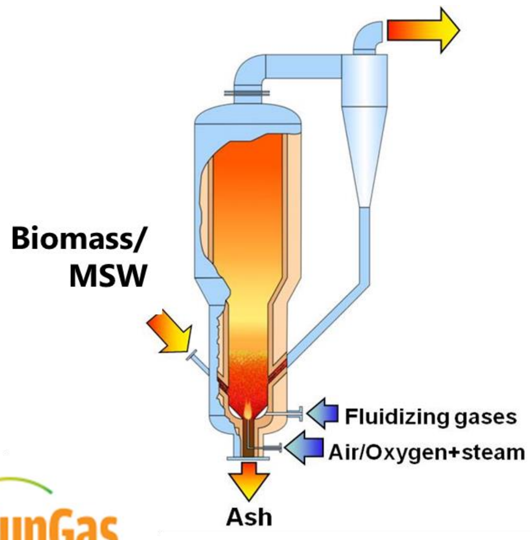
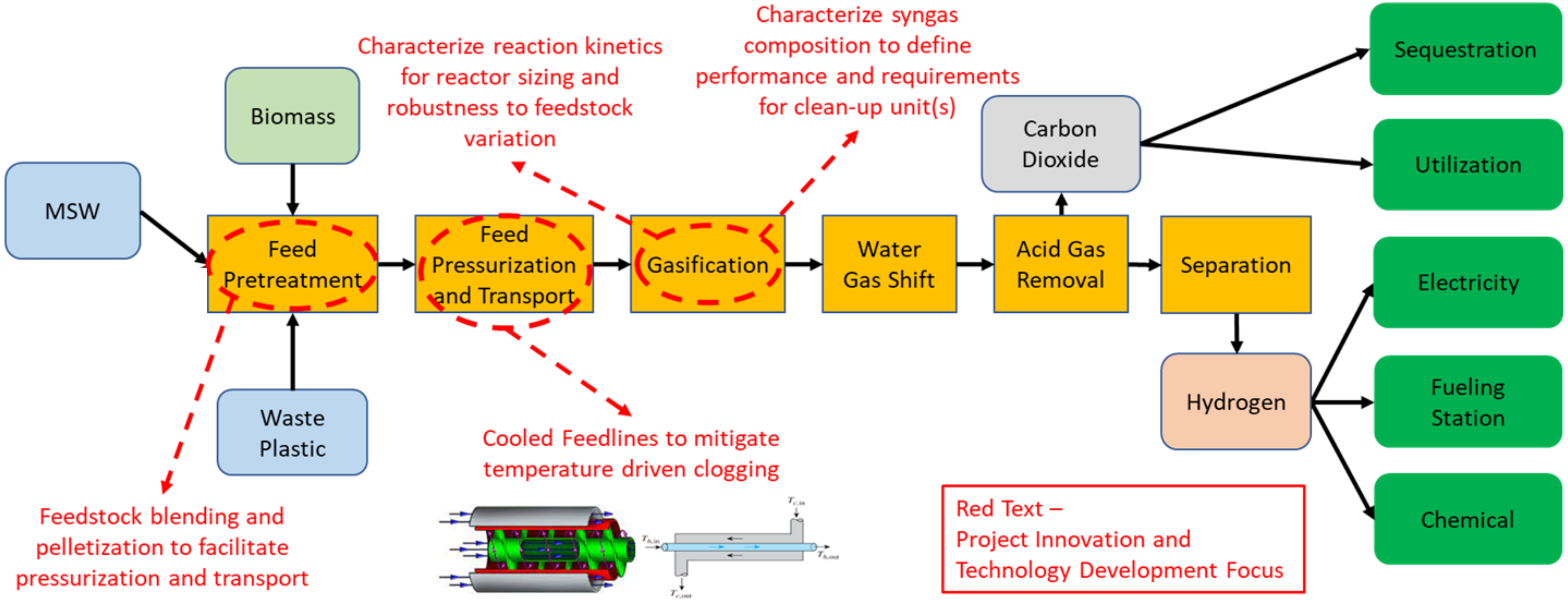
## U-GAS



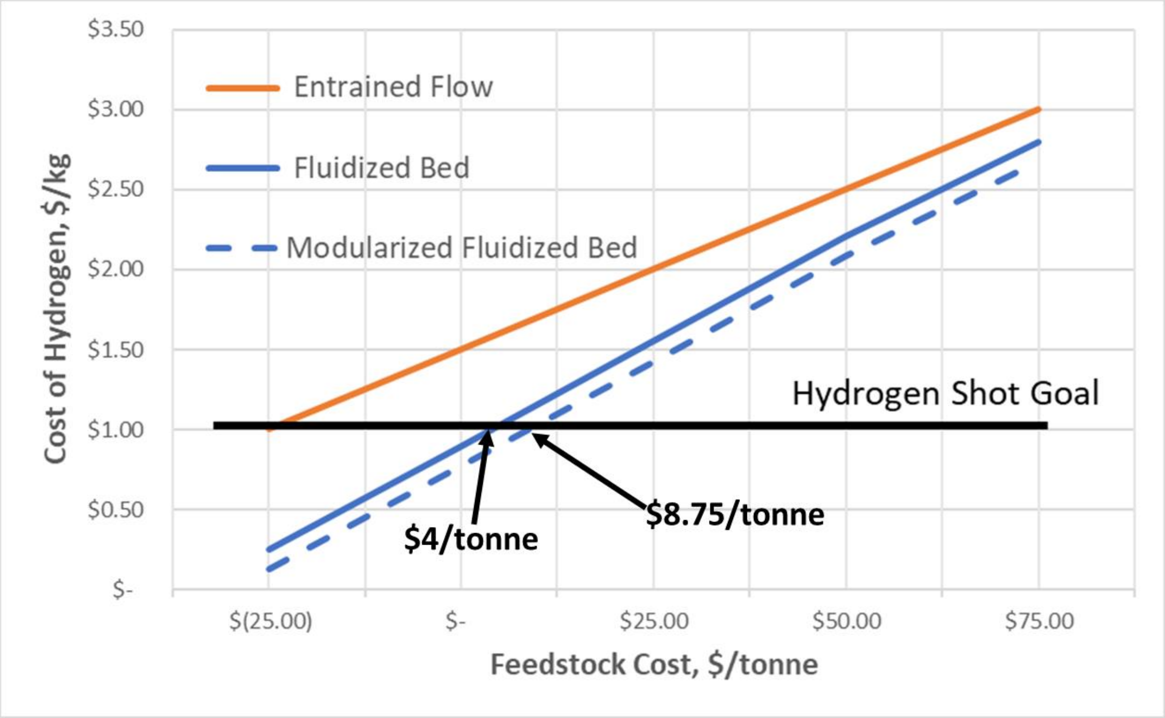

SunGas RENEWABLES

**Commercially offered by SunGas Renewables for biomass applications**




- Gasification pathway advancements to enable zero emission conversion of waste feedstocks - progression to TRL5

# Project Concept – Leverage both Biomass and MSW




- $1/kg of hydrogen is achievable with combined feedstock costs below $8.75/tonne
- Challenges:
  - **Biomass** can reduce process carbon intensity, but is far too expensive ($75-150/ton)
  - **MSW** could generate a considerable tipping fee (~$58/ton) but is heterogeneous, hard to handle, and contains plastics
  - Characterization, ash properties, handling, blending and feeding issues?
- **Project objectives:** Feedstock characterization and pre-treatment, pressurization/injection into bed, gasification

# Feedstock Procurement and Preparation

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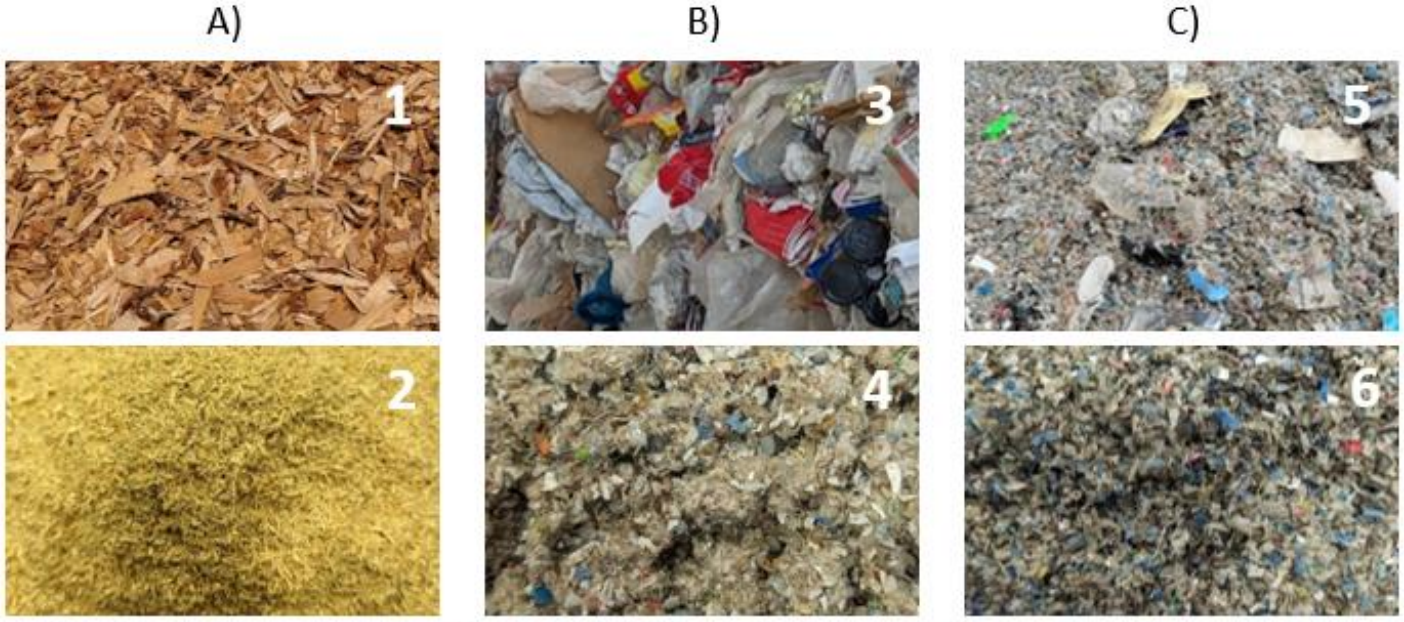
- Biomass: Loblolly Pine, Southern Georgia, USA
- MSW: Recycle Ann Arbor, MI.
  - Only paper and plastic fractions
- Plastics:
  - 90 wt%: “waste plastic” from EFS Plastic in Ontario, Canada
  - 10 wt%: film plastic - meat packaging - Sealed Air Corporation, SC



As received

After grinding




A) Biomass (Loblolly pine), B) MSW; C) Plastic.

Example Pellets:

Biomass (50%): MSW (50%)

Biomass (50%): Plastic (50%)

Biomass (50%): MSW (25%): Plastic (25%)

# Feedstock Analysis

- Plastics content of MSW and "Plastics" samples not compatible with equipment and protocols
- Significant differences between biomass ash and ash from the two other feedstock types

| Sample ID | | Biomass | | MSW | | Plastic waste | |
|---|---|---|---|---|---|---|---|
| **Proximate Analysis result (wt.%)** | | | | | | | |
| | Method | adb[1] | db[2] | adb | db | adb | db |
| **Inherent moisture content** | ISO 11722: 2013 [5] | 5.4 | – | 1.5 | – | 0.9 | – |
| **Ash yield** | ISO 1171: 2010 [6] | 1.0 | 1.0 | 12.7 | 12.9 | 7.8 | 7.9 |
| **Volatile matter content** | ISO 562: 2010 [7] | 81.1 | 85.8 | 81.1 | 82.3 | 87.2 | 88.0 |
| **Fixed carbon content** | By difference | 12.5 | 13.2 | 4.7 | 4.8 | 4.1 | 4.1 |
| **Ultimate analysis (wt.%)** | | | | | | | |
| **Carbon content** | ISO 17247: 2020 [8] | 48.2 | | | | | |
| **Hydrogen content** | ISO 17247: 2020 [8] | 5.9 | | | | | |
| **Nitrogen content** | ISO 17247: 2020 [8] | 0.17 | | | | | |
| **Sulphur content** | ISO 19579: 2006 [9] | N.D[3] | | | | | |
| **Oxygen content** | By difference | 39.4 | | | | | |
| **Cl and F elemental analysis (mg/kg)** | | | | | | | |
| **Chlorine** | | 96 | | | | | |
| **Fluoride** | | < 50 | | | | | |
| **Bulk density (kg/m³)** | | | | | | | |
| Bulk density | | 228.3 | | 183.3 | | 145.8 | |

*[1]-adb- Air dry basis; [2]-db- Dry basis, [3]- Not determined*

| Sample ID / Properties | Biomass ash | MSW ash | Plastic waste ash |
|---|---|---|---|
| Ash fusion temperatures (oxidising atmosphere) (°C) | | | |
| Initial deformation temperature | 1190 | 1130 | 1160 |
| Sphere temperature | 1210 | 1150 | 1170 |
| Hemispherical temperature | 1250 | 1190 | 1180 |
| Flow temperature | 1310 | 1210 | 1210 |
| Ash fusion temperatures (reducing atmosphere) (°C) | | | |
| Initial deformation temperature | – | 1120 | 1140 |
| Sphere temperature | – | 1140 | 1150 |
| Hemispherical temperature | – | 1180 | 1160 |
| Flow temperature | – | 1210 | 1190 |
| XRF results (wt.%) | | | |
| $Al_2O_3$ | 31.69 | 10.09 | 10.38 |
| $CaO$ | 5.19 | 17.64 | 20.64 |
| $Cr_2O_3$ | 0.03 | 1.83 | 0.89 |
| $Fe_2O_3$ | 3.63 | 8.61 | 5.56 |
| $K_2O$ | 0.63 | 0.42 | 0.65 |
| $MgO$ | 2.03 | 1.90 | 4.36 |
| $MnO$ | 0.03 | 0.18 | 0.13 |
| $Na_2O$ | 0.15 | 7.16 | 5.68 |
| $P_2O_5$ | 0.92 | 0.36 | 0.38 |
| $SiO_2$ | 48.65 | 48.20 | 45.88 |
| $TiO_2$ | 1.51 | 2.34 | 3.51 |
| $V_2O_5$ | 0.05 | 0.01 | < 0.005 |
| $ZrO_2$ | 0.09 | 0.01 | 0.02 |
| $BaO$ | 0.25 | 0.07 | 0.20 |
| $SrO$ | 0.24 | 0.02 | 0.04 |
| $ZnO$ | 0.02 | 0.09 | 0.16 |
| $SO_3$ | 4.73 | 0.54 | 0.51 |
| Loss on ignition | 0.16 | 0.53 | 1.00 |

# Feedstock Tar Characterization

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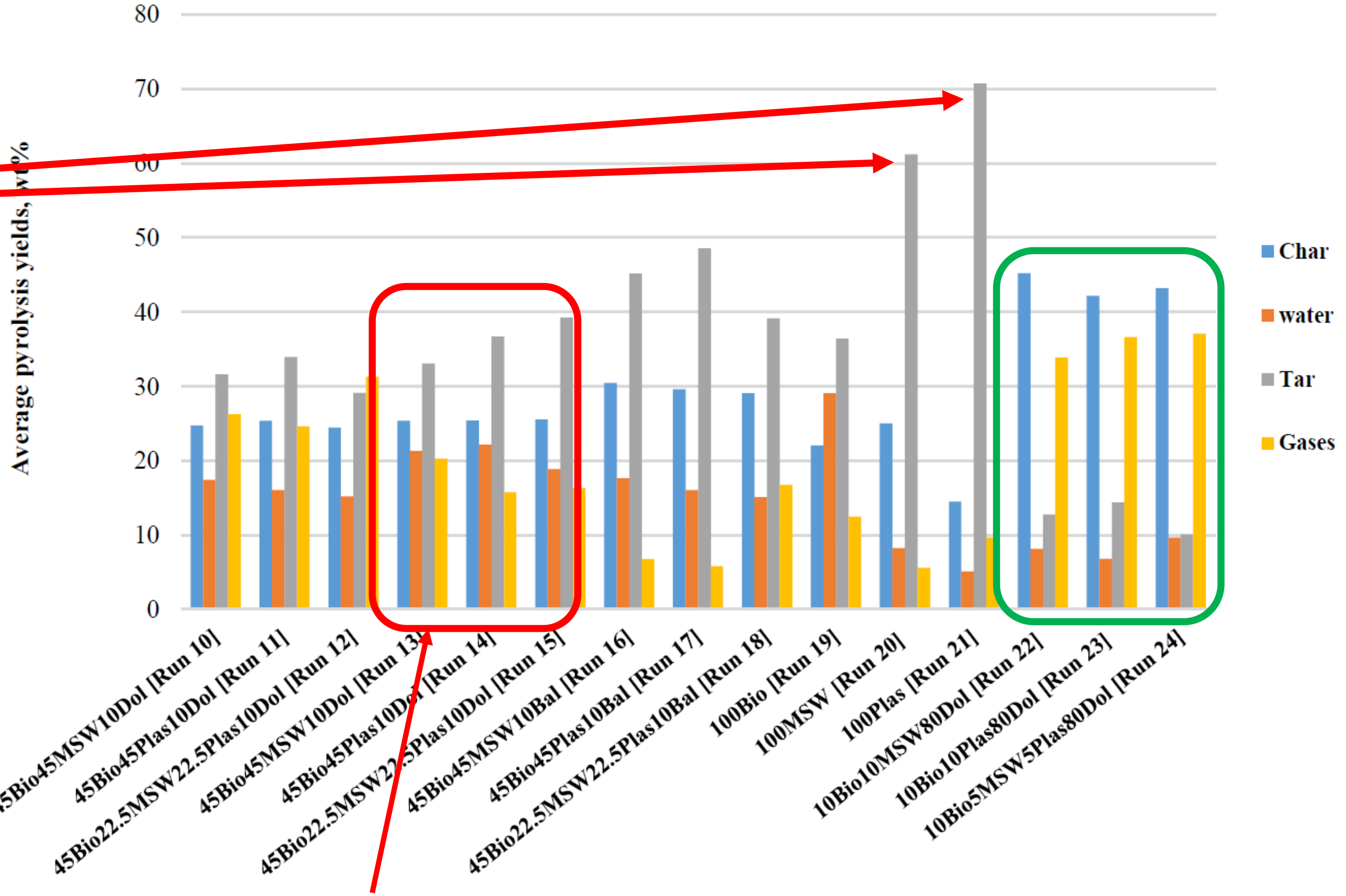
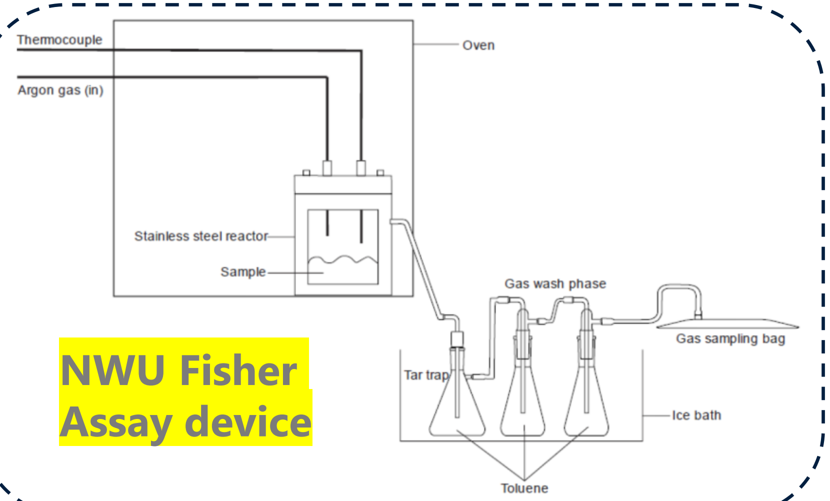
- Work conducted at Northwest University (NWU) in South Africa
- High production of tars from 100% MSW and 100% Plastics feedstocks.
- **Loaded 80% by mass catalyst in Runs 22-24; tar yield dropped! Char yield increased – promising indication**



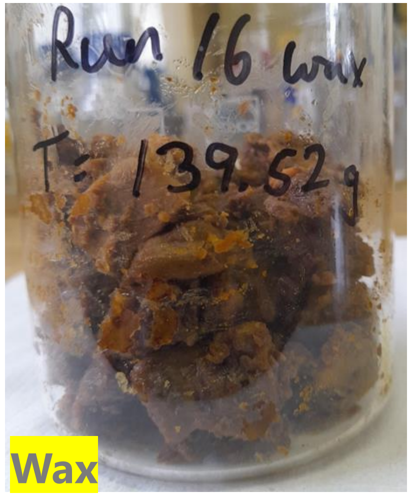




NWU Fisher Assay device

Note: Runs 13, 14, and 15 were carried out at temperatures up to 850 C to match usual U-Gas bed temperatures. All other runs in this series were at 950 C following usual NWU protocol

# Feedstock Pyrolysis

- Work conducted at Innoventon lab in South Africa
- Innoventon subjected the pellet samples to a devolatilization protocol (to 650 °C), using various amounts of feedstock pellets and bed material (brown alumina or dolomite)
- The goal of the pyrolysis was to produce char and ash materials from the various feedstocks to be then tested for reactivities using a thermo-gravimetric analyzer (TGA).

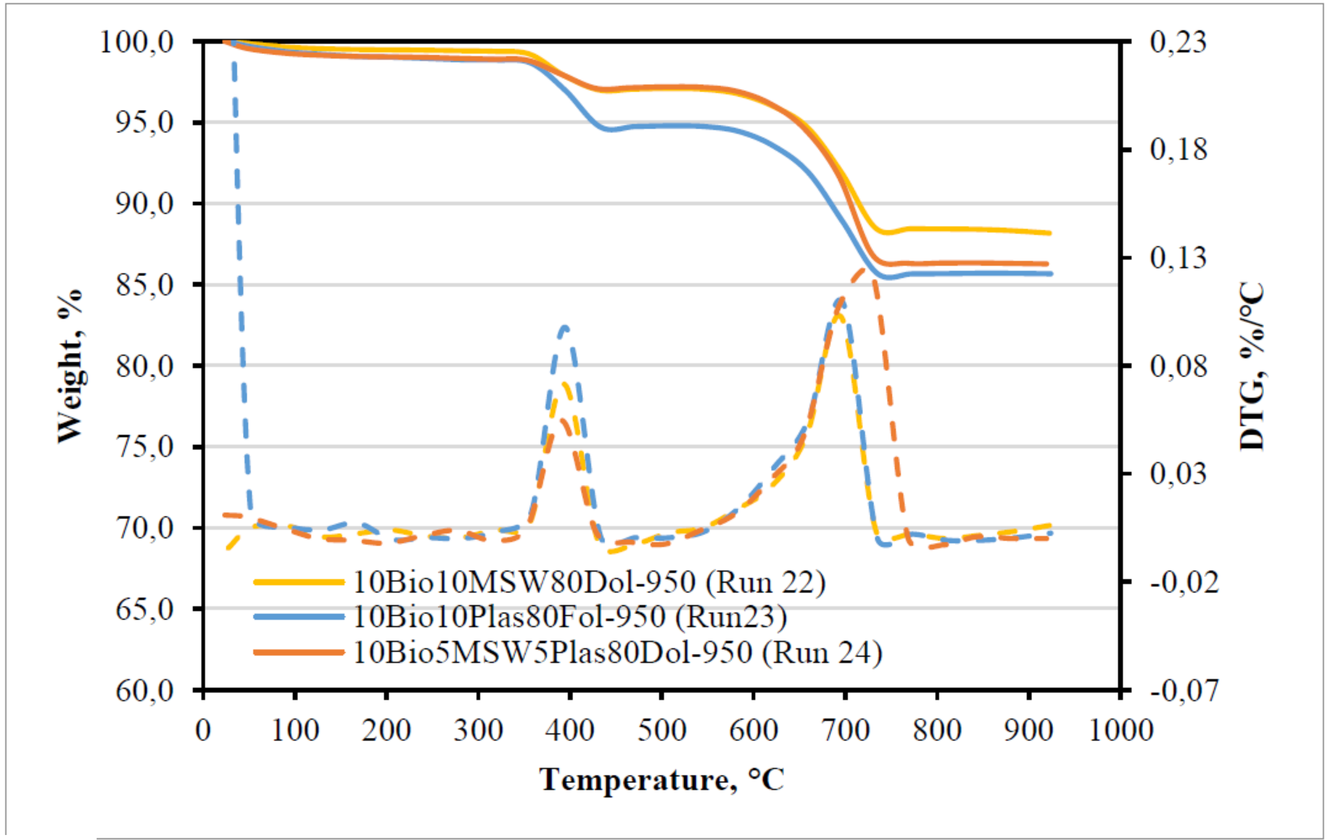





# Feedstock TGA

- Work performed at NWU
- NWU CO2 Reactivity TGA – carried out in connection with all chars produced from the pyrolysis work at Innoventon.
- The CO2 Reactivity TGA curves associated with chars from all three runs displayed a unique two-step mass loss trend – sequential reaction of different types of compounds comprising the char/coke on the bed material

NWU TGA




TGA pyrolysis mass loss curves of blends of runs 22 – 24.

# Feedstock Bench-scale Gasification

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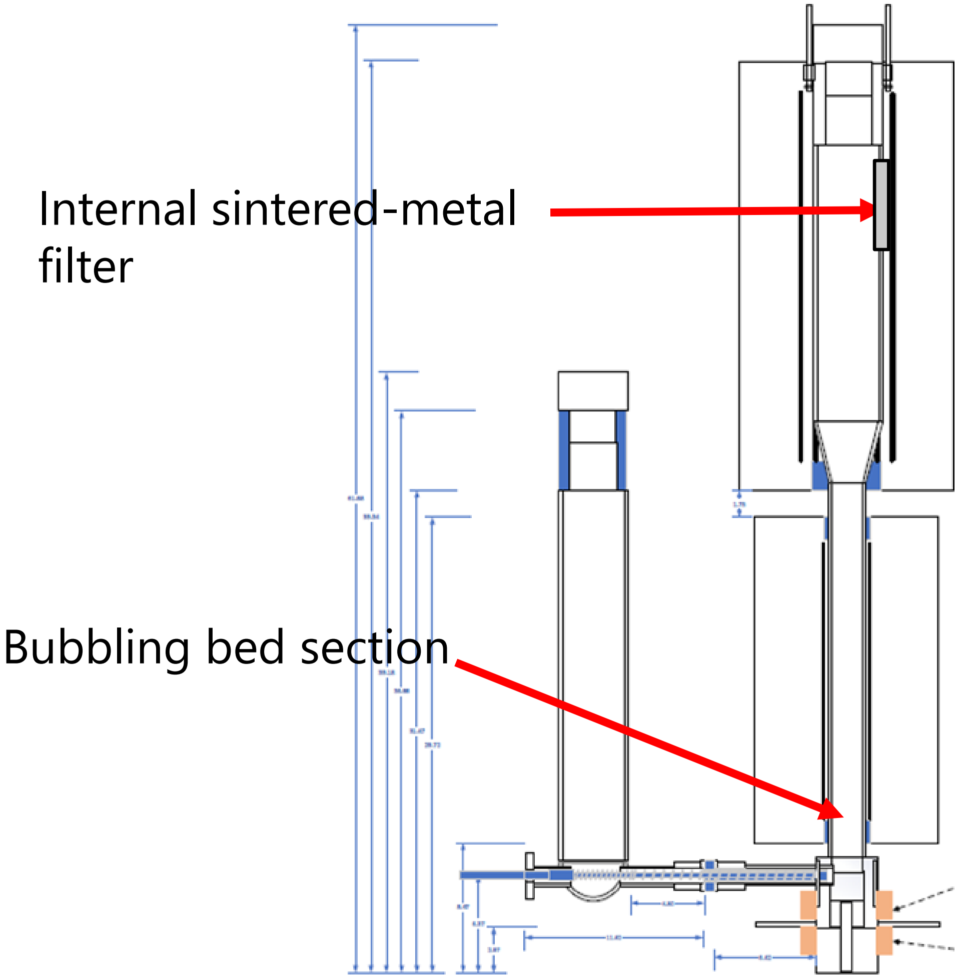
- Work performed in the Mini-bench Unit Gasifier (MBU-G) fluidized-bed gasifier at the GTI Energy campus in Des Plaines, IL.
- Data from South African laboratories indicated that:
  - There was little functional difference between our MSW and Plastics feedstocks – high plastics content in both, similar ash content
  - Both the MSW and Plastics feedstocks were likely to produce very high yields of tars when devolatilized – possible operational problems
  - Very low fixed carbon in all three primary feedstocks – not a problem for U-GAS, though
  - Contacting with large amounts of bed material during devolatilization might react away tar and help produce clean syngas
  - An 800-850 C was likely hot enough to fully react feedstock without melting ash (slag) – desired for U-GAS

# MBU-G Operation Summary

- Dolomite (industrially-relevant), Bed depth ~24” once fluidized (-80+120 Mesh)
- Dolomite was baked out at 1000 F before loading
- 2” Sched 40 pipe high-temp alloy lower section
- 4” Sched 40 pipe disengagement section
- Feed rate 7-10 grams/minute of feedstock
- 50 psig operating pressure; fluidized via N2 and steam
- Sintered-metal filter located inside vessel to remove fines
- Bed target temperature 815 C (1500 F)



# MBU-G Test Plan



- Received three INL pellet sample formulations, bought a fourth type of pellet (commercial hardwood for shakedown) – crushed/sieved
- Highly successful series of four experiments
  - 8/16/2023: Shakedown – commercial hardwood pellets
  - 9/12/2023: 50/50/0 (INL Pine Biomass-MSW Pellet fragments)
  - 09/29/2023: 100/0/0 (INL Pine Biomass pellet fragments)
  - 10/05/2023: 50/25/25 (INL Pine Biomass-MSW-Plastics pellet fragments)

# MBU-G Feedstocks Analysis

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| | 100% Biomass - Shakedown | 50% Biomass – 50% MSW | 100% Biomass | 50% Biomass – 25% MSW – 25% Plastics |
|---|---|---|---|---|
| Feedstock Proximate Analysis (as-received basis) | | | | |
| Moisture (107°C) wt%: | 6.1 | 6.45 | 7.25 | 4.08 |
| Volatile matter as rec'd wt%: | 80.1 | 77.91 | 79.62 | 81.6 |
| 750°C ash as rec'd wt%: | 0.5 | 6.63 | 0.72 | 6.59 |
| Fixed carbon (by diff.) wt%: | 13.4 | 9.01 | 12.41 | 7.73 |
| | | | | |
| **Feedstock Ultimate analysis (dry basis), no SO3 correction on ash** | | | | |
| **750°C ash dry basis wt%** | **0.5** | **7.09** | **0.78** | **6.9** |
| **Carbon dry basis wt%** | **49.6** | **55.71** | **50.07** | **55.16** |
| **Hydrogen dry basis wt%** | **6.0** | **7.3** | **6.16** | **7.21** |
| **Nitrogen dry basis wt%** | **0.2** | **0.12** | **0.25** | **0.28** |
| **Sulfur dry basis wt%** | **0.0** | **< 0.01** | **0.03** | **0.09** |
| **Oxygen dry basis wt%** | **43.7** | **29.78** | **42.71** | **30.36** |
| **Bromide dry basis ug/g** | **-** | **<69** | **<65** | **<67** |
| **Chloride dry basis ug/g** | **-** | **2943.0** | **733** | **3184** |
| **Fluoride dry basis ug/g** | **-** | **<69** | **97** | **<67** |

# MBU-G Yield Profiles

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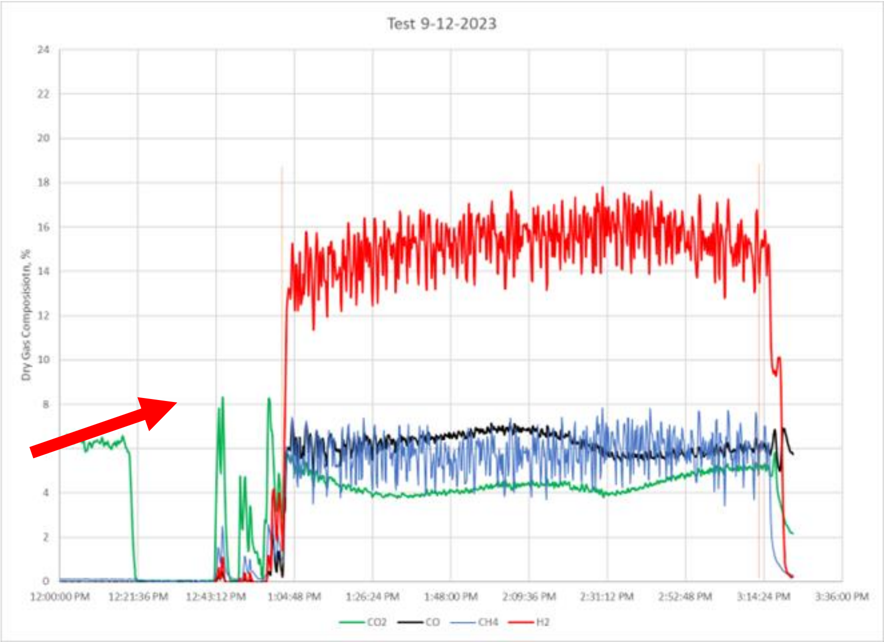
| Date: | 100% Biomass - Shakedown | 50% Biomass – 50% MSW | 100% Biomass | 50% Biomass – 25% MSW – 25% Plastics |
|---|---|---|---|---|
| Approximate Mass Balance Closure: (Products/Reactants), %: | 95.8 | 99.9 | 101.9 | 100.3 |
| | | | | |
| Gas Bomb H2:CO Molar Concentration Ratio: | 2.1 | 1.7 | 1.7 | 2.0 |
| | | | | |
| Yield profile as mass % of feedstock mass: | | | | |
| | | | | |
| Char, % | 0 | 6.2 | 0.0 | 6.9 |
| Hydrogen, % | 5.1 | 4.4 | 5.6 | 4.0 |
| Carbon Dioxide - BY DIFFERENCE, % | 50.1 | 28.0 | 42.2 | 33.5 |
| Carbon Monoxide, % | 34.0 | 35.6 | 45.3 | 28.5 |
| Methane, % | 7.3 | 9.3 | 5.6 | 9.7 |
| Ethane, % | 0.6 | 2.0 | 0.2 | 1.6 |
| Ethene, % | 1.8 | 7.0 | 1.1 | 6.2 |
| Hexanes Plus, %: | 1.0 | 7.5 | 0.0 | 9.5 |

50/50/0 (INL Biomass-MSW Pellet fragments) – optimal pellet composition (carbon intensity and economics), promising MBU-G results – **chose this 50/50 pellet formulation for pilot-scale feed testing**

# MBU-G - 50% Biomass – 50% MSW Trends

- 50% Biomass – 50% MSW Pellet fragments -4+14 Mesh
  - This pellet formulation allows for “carbon-negative” operation at the lowest feedstock cost
  - N2 (fl. gas). Steam. **Air O2-to-C = 0.14:1**
  - **Steam-to-carbon ratio: 0.4:1**
  - Targeted 0% O2 in effluent gas while maintaining bed temperature
  - Online and offline (GC) gas analysis and ETP
  - **NO PROBLEMS WITH TARS – deep bed of dolomite removed tars and prevented deposits in filters, lines, etc.**

| | |
|---|---|
| H2: | 12 % |
| CH4: | 3.1 % |
| CO: | 6.9 % |
| CO2: | 4.6 % |



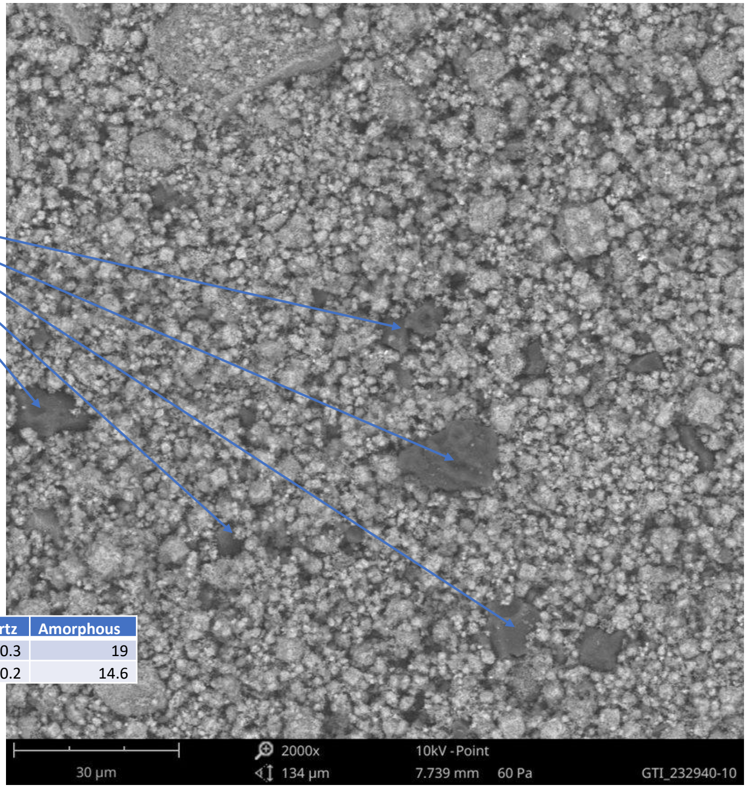

Investigated high H2/CO ratio – found no issues with instrumentation or experimental conditions

# MBU-G Ash Analysis

- XRD and SEM Analyses concluded:
  - Both crystalline and amorphous phases were detected, with a ratio of 95:5 mass %.  This was as expected with localized slag formation from the low melting material such as  biomass
  - The bed material (dolomite) was partially transformed and decomposed to CaO and CO2 and partially un-transformed.  The operating temperature of the MBU was as such and on the border of the transformation range, i.e. around 850 °C

Bulk of structure mineral / crystalline

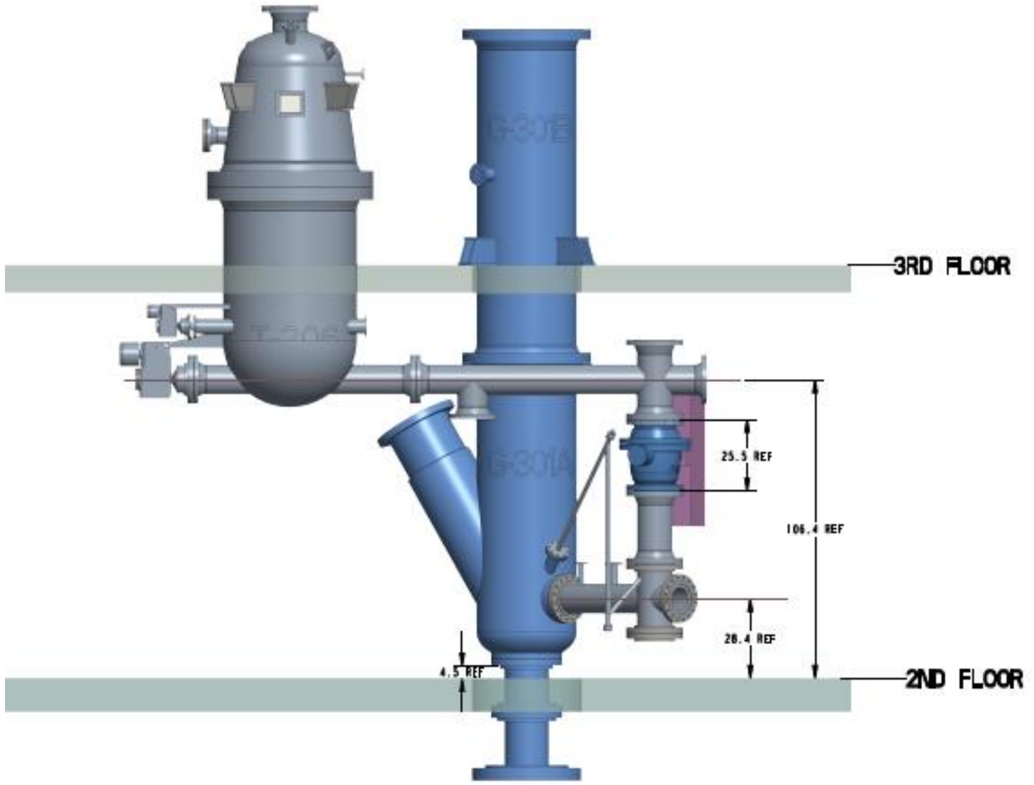
Localized slag and amorphous droplets




| | Lime | Periclase | Portlandite | Calcite | Dolomite | Quartz | Amorphous |
|---|---|---|---|---|---|---|---|
| GTI_232940-007 | 17.3 | 32.5 | 3.8 | 26.2 | 0.8 | 0.3 | 19 |
| GTI_232940-10 | 35 | 36.5 | 1.6 | 9.4 | 2.6 | 0.2 | 14.6 |

# Pilot Scale U-GAS Feed System Testing

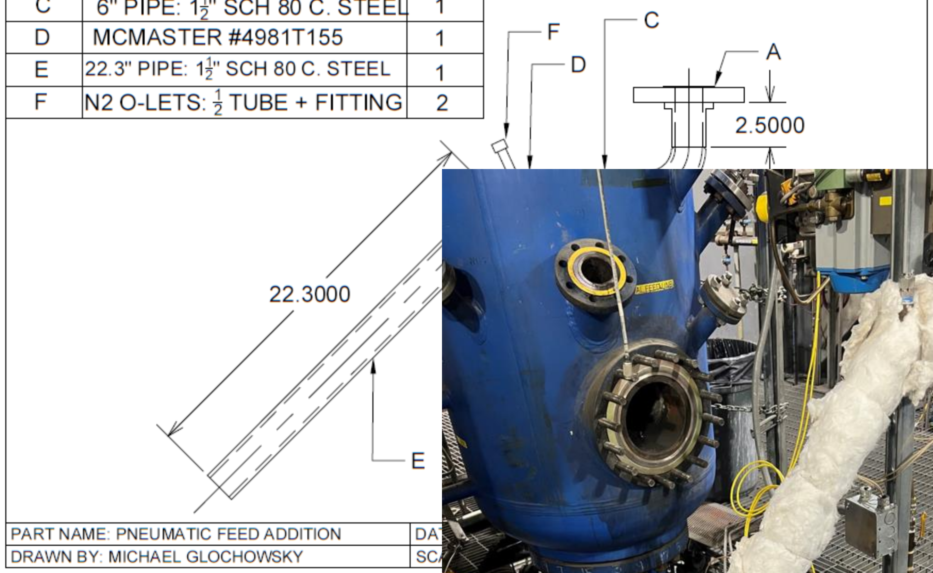
- Both the pilot U-GAS pneumatic feed and mechanical screw feed configurations have been tested.

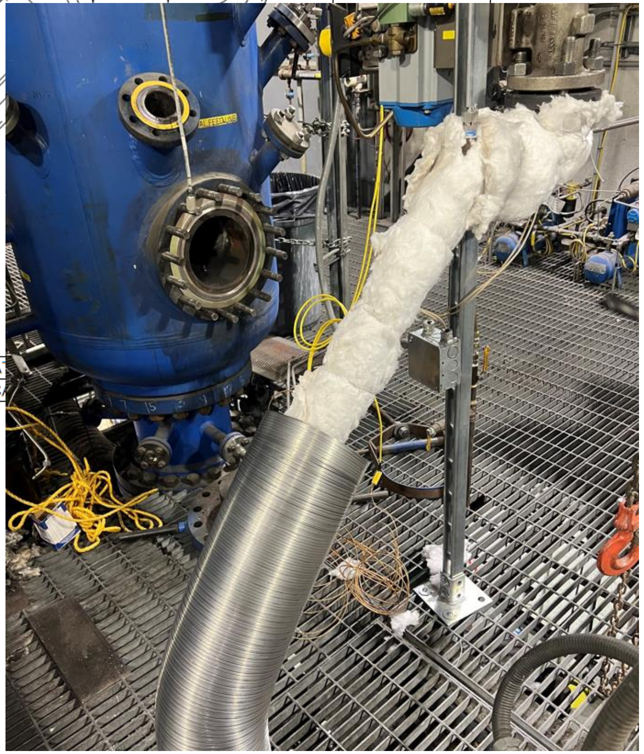



# Pilot Scale U-GAS Pneumatic Feed System Testing

- Tested U-GAS Pneumatic feedstock injector
- GTI modified the pneumatic transfer pipe to accommodate pellets instead of powders – added electrical heating to simulate U-GAS operational conditions/pellet softening
- Supplied maximum transport gas velocity allowed by established U-GAS protocols
- Higher gas velocities not compatible with fluidization regime of the bed => excessive local cooling
- Pellets are simply too large – not mobile at relevant gas velocities – definitive result
- Did not heat the pneumatic feeder outlet during these tests – ambient temperature only

| ID | DESCRIPTION | QTY. |
|---|---|---|
| A | $1\frac{1}{2}$" 300# SA/A182 C. STEEL B16.5 BA38 FLANGE | 1 |
| B | MCMASTER #4981T15 | 1 |
| C | 6" PIPE: $1\frac{1}{2}$" SCH 80 C. STEEL | 1 |
| D | MCMASTER #4981T155 | 1 |
| E | 22.3" PIPE: $1\frac{1}{2}$" SCH 80 C. STEEL | 1 |
| F | N2 O-LETS: $\frac{1}{2}$ TUBE + FITTING | 2 |



# Pilot Scale U-GAS Screw Feed System Testing

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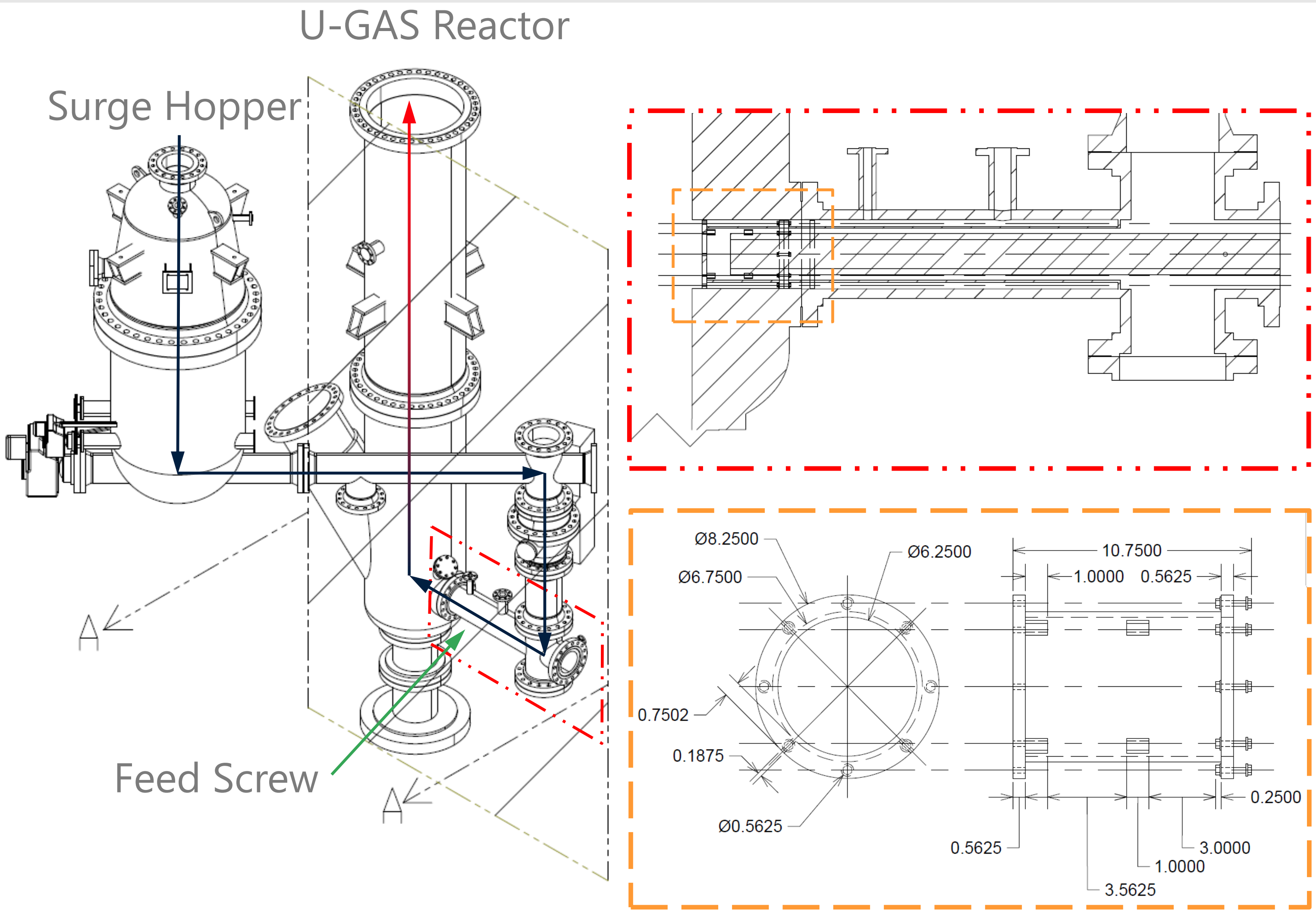
- 40 rpm, pellets design rate 1200 lbs/hr
- Screw assembly features a 310 SS shroud at the front end – feedstock passes through the shroud and into the bed of the gasifier
- The screw was re-oriented to move feedstock pellets without sending them into the U-Gas vessel
- Electrical heating system and insulation installed around the shroud – up to 500 F operating temperature available – 1254 W of heating
- Objective: identify temperature at which pellets soften, disintegrated and/or agglomerate in the shroud
- Excellent results: Even at ~500 F, no effect of heating on feedstock was noted – tested 1200 lb/hr down to 300 lb/hr; no change in pellet morphology at any of the temperatures tested


# Cooled Shroud Design

- Purpose
  - Design a shroud modification to ensure shroud tip does not exceed 350°C - Avoid feedstock softening and plugging injector screw



# Next Development Steps for U-GAS

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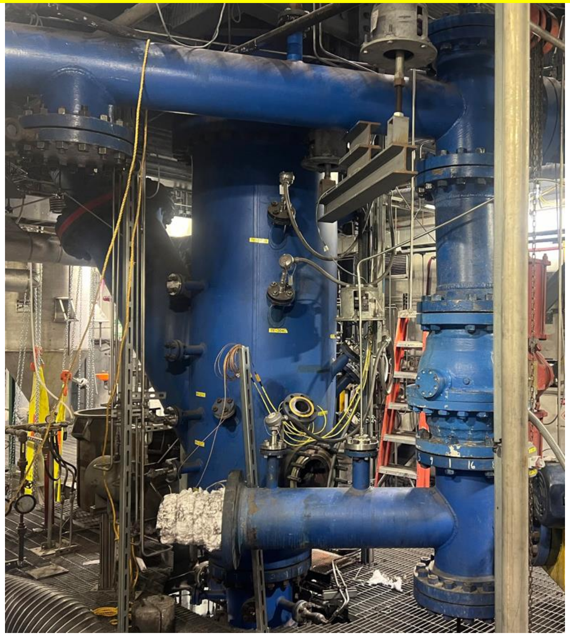
- Biomass and MSW pellets (50% / 50%) benchtop gasification work has been successfully demonstrated at the GTI Energy fluidized bed mini-bench unit gasifier (MBU-G) under project DE-FE0032176.
- Pilot-scale feeding of mixed biomass and MSW pellets (50% / 50%) has been successfully demonstrated at the U-GAS pilot-scale facility under project DE-FE0032176.
- Technology is ready to move on to pilot-scale gasification testing!! → Establish pathway to produce net zero $H_2$ at $1/kg.

**Define Supply Chain for 50% Biomass / 50% MSW pellets**

→

**500 hours of Pilot gasification testing**



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**Commercial System Optimization Study**

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*solutions that transform*

GTI Energy develops innovative solutions that transform lives, economies, and the environment